

Screening Method for Nitroaromatic Compounds in Water Based on Solid-Phase Microextraction and Infrared Spectroscopy

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A new method is described for determining nitroaromatic compounds in water that combines solid-phase microextraction (SPME) and infrared (IR) spectroscopy. In this method, the compounds are extracted from a 250-mL volume of water into a small square (3.2 cm \times 3.2 cm \times 61.2 μ m thick) of silicone polycarbonate copolymer film (MEM-213). Five nitroaromatic compounds, including 2,4,6-trinitrotoluene (TNT), were chosen to evaluate the SPME/IR procedure. Quantitation limits for the five test compounds range from 50 μ g/L for TNT to 400 μ g/L for nitrobenzene. Precision values, determined at aqueous concentrations of four times the quantitation limit, range from 4 to 7%, and linear dynamic ranges extend to the maximum limit of the IR instrumentation. The potential of this SPME/IR method for determining nitroaromatics in natural water samples was also investigated by extracting "real world" soil samples contaminated with TNT. Results obtained from the SPME/IR determination of the diluted extracts were in reasonable agreement with those obtained from dichloromethane extraction followed by gas chromatographic analysis.

Introduction

The determination of nitroaromatic compounds (e.g., trinitrotoluene explosives and dinitrotoluene propellants) in soil and water is required by several U.S. agencies in order to establish their presence and concentration. Many nitroaromatics are quite persistent in these matrices under ambient conditions, and high-density sampling is often required since some of these compounds are also heterogeneously distributed. Standard methods for determining these organics in environmental matrices generally involve an extraction step (liquid–liquid extraction (LLE) or solid-phase extraction (SPE)) followed by analysis with gas or liquid chromatography. Although each of these methods has certain advantages and disadvantages, many of them are time-consuming, labor-intensive, and require relatively expensive instrumentation. In addition, most are not readily adaptable to field determinations. Field determination is attractive because it eliminates many of the problems connected with collecting and transporting samples (e.g., representative sampling, contamination, loss of volatiles, storage, etc.), and it provides immediate results. Thus, simpler, more economical methods are needed for field screening and monitoring of containment and remediation operations.

One approach in the search for simple and field-portable analytical methods involves adapting immunoassay-based technology. Immunoassay methods measure analytes by using an antibody specific to the compound of interest. The most recent technological developments in this field include the continuous-flow immunosensor (1) and fiber-optic biosensor (2, 3). Both techniques involve competitive displacement of a fluorescent analogue from a solid support of antibodies. A change in the fluorescence signal resulting from displaced analogue is thus proportional to the concentration of analyte in the sample. These methods have been developed specifically for detection of explosive compounds such as 2,4,6-trinitrotoluene and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). Although the immunoassay techniques are quite sensitive (detection limits as low as 5 μ g/L for TNT), there is a degree of cross-reactivity among compounds of similar structure. For example, 1,3,5-trinitrobenzene and dinitrotoluene produce a positive response in an assay for TNT. Matrix interferences have also been observed in the analysis of some natural water samples.

Colorimetric methods, often used in field determinations, are nonimmunoassay tests that generally detect broad classes of compounds such as nitroaromatics or nitramines. An assay developed for nitroaromatic compounds results in the formation of a red-colored anion by adding potassium hydroxide base to an acetone extract of soil (4, 5). A variation of this assay that is more specific for TNT utilizes sodium hydroxide base in a methanol extract of soil (6). The resultant anion appears pink to purple in color. Nitramines in soil are detectable by the formation of a reddish Azo dye (5–7). This assay, however, requires that nitrate and nitrite ions first be removed by anion exchange. The formation of colored products can be determined either visually or with a spectrometer. These methods are, however, susceptible to matrix interference from humic substances that are present in soil.

In this work, we describe a simple method for the detection of nitroaromatic compounds that combines solid-phase microextraction (SPME) with infrared transmission spectroscopy (SPME/IR). Solid-phase microextraction involves the selective partitioning of organic compounds from a matrix into a chromatographic solid phase (8). Recently, SPME has been coupled with gas chromatography/ion trap mass spectrometry to obtain extremely low detection limits for RDX, TNT, and the amine transformation products of TNT in seawater (9). This extraction technique utilized a syringe device in which solid phase was coated onto a short length of glass fiber. Although the method is rapid and sensitive, there are difficulties with precision and accuracy. The mass spectrometer is also not a field-portable instrument.

Our application of the SPME technique utilizes a small square of silicone polycarbonate copolymer film for the solid phase. Infrared (IR) absorbance spectra of the copolymer films containing the extracted analytes are then used to obtain quantitative data. Infrared spectroscopy is a powerful tool for the identification of molecular structure. Since each of the nitroaromatic compounds discussed above has a unique infrared spectrum, it potentially may be used as a "fingerprint" for the molecule. IR spectrometry is more sensitive and selective than colorimetric methods and does not require the use of mass spectrometry or antibody-based equipment. Additionally, IR spectrometry is fast, relatively inexpensive to implement, has rugged instrumentation, and analytes can be easily quantitated through the Beer–Lambert law ($A = \epsilon bc$, where A is the absorbance, ϵ is the molar absorptivity, b is the path length, and c is the concentration). As an added

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advantage, the SPME/IR method is able to determine the presence of the 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene transformation products. These compounds are not detectable by current immunoassay or colorimetric methods (10).

Experimental Section

Extraction Films and Apparatus. The polymer solid phase used for the extraction procedure was a commercially available silicone polycarbonate copolymer film of 38.1- μm (0.0015-in.) thickness obtained from Membrane Products Co. (Salt Lake City, UT). The bulk film sheet was cut into 32-mm squares with a resultant calculated volume of 39 mm³ per square. Film pieces of greater thickness were created by heat-sealing two of the squares together. The squares were first positioned between two metal disks (commercially available as nailing disks used in the roofing industry), and the disks were then placed between two pieces of glass. This assembly was secured with a c-clamp and placed in a drying oven at 100 °C for 1 h. The 7-cm diameter metal disks and 7.5-cm square glass pieces were purchased from a local building supply store. Each film square was dry sanded prior to use with 320-grit wet/dry sandpaper in four different directions on both sides. The films were further conditioned by rinsing in a solution of methanol and water (50:50) for 15 min to increase the extraction efficiency. Membrane Products Co. no longer sells the silicone polycarbonate copolymer membrane. The new manufacturer is Specialty Silicone Products, Inc. (Ballston Spa, NY). It is now marketed as SSP-M213 and is available in thicknesses ranging from 12.7 μm (0.0005 in.) to 102 μm (0.004 in.).

Metal holders were made to support the PFA film during the extraction procedure and in acquiring the IR spectra. The holder consisted of a 14-gauge steel plate 44.5 mm long and 51 mm wide with a 19.1-mm diameter hole in the center corresponding to the IR aperture (11). The film was secured to the metal plate over the hole with a ceramic ring magnet of 25-mm inner diameter and 35-mm outer diameter (Cenco – Central Scientific Co., Franklin Park, IL). Two screws inserted in holes drilled near the bottom of the plate provided support for the magnet and prevented it from slipping during extraction.

Glass jars with Teflon-lined lids (250-mL volume) were used as the extraction vessels (Cole-Parmer, Vernon Hills, IL). Each vessel was modified by drilling two holes through the lid and inserting 18-gauge wire to form a hook. The holes were sealed on the exterior of the lid with silicon sealant. A small hole near the top of the metal plate provided a means of suspending the film holder assembly from the lid of the jar into the aqueous solution.

Reagents and Samples. The 2,4,6-trinitrotoluene, 4-amino-2,6-dinitrotoluene, 2-amino-4,6-dinitrotoluene, and hexahydro-1,3,5-trinitro-1,3,5-triazine were purchased from Chem-Service (West Chester, PA). The 2,4-dinitrotoluene was purchased from Aldrich Chemical Co. (Milwaukee, WI). Nitrobenzene and 2-nitrotoluene were obtained from Fisher Scientific (Pittsburgh, PA) and Eastman Chemicals (Kingsport, TN), respectively. Gas chromatography (GC) grade dichloromethane (CH_2Cl_2) was obtained from EM Science (Gibbstown, NJ).

Standard stock solutions were prepared by first dissolving the appropriate amount of compound in methanol and then diluting with distilled water in a volumetric flask. The final methanol concentration did not exceed 0.4% of the solution volume. Calibration standards were prepared in volumetric flasks by diluting aliquots from the stock solutions with distilled water. Aqueous standard solutions were analyzed within an 8-h time period following preparation.

Spiked solutions of 2,4,6-trinitrotoluene and 4-amino-2,6-dinitrotoluene were prepared in natural water obtained

from a local drainage channel. Three replicate 500-mL volumes were prepared for each spike concentration level. A 250-mL aliquot of each solution was analyzed by SPME/IR, and the remaining 250-mL volume was extracted with dichloromethane for GC analysis.

Two soil samples known to contain explosive compounds were donated by a researcher associated with the University of North Dakota. One of the samples was contaminated with 10–12% TNT. The other sample was contaminated with 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) and RDX (0.32% and 0.075% respectively). Both soil samples were extracted, and the extracts were diluted with distilled water for analysis.

Infrared Spectrometry. The IR spectra were acquired on an ATI Mattson Genesis FTIR spectrometer (Madison, WI) equipped with a room temperature, deuterated triglycine sulfate detector (DTGS). All spectra were obtained at a scan rate of 6.25 kHz, with a 4 cm^{-1} resolution. The spectrometer used a triangular phase apodization function and 2X zero-filling. Sixty-four scans were signal-averaged for both the sample and background spectra. Savitzky-Golay smoothing was applied to the absorbance data with a 19-point quintic polynomial method used to determine the weighting factor. This instrument operates in a WinFirst software framework.

Gas Chromatography. Reference analyses for the spiked water samples were performed using a Hewlett-Packard 5890 Series II gas chromatograph with flame ionization detection. The GC was equipped with a 30-meter DB-5 capillary column of i.d. 0.32 mm and a film thickness of 0.25 μm (J&W Scientific, Folsom, CA). Dichloromethane solutions and extracts were manually introduced into a standard split/splitless injector using the splitless mode. The purge valve remained closed for 1 min following injection, and the GC oven was held at 50 °C during that time. The temperature was subsequently ramped to 280 °C at 12 °C/min and held at 280 °C for 1 min. Injector and detector temperatures were 280 °C and 320 °C, respectively. Injection volumes were all 1 μL .

SPME Extraction Procedure. Prior to extraction, a single-beam IR spectrum of each copolymer film was acquired to serve as a background reference. The copolymer film/holder assembly was then attached to the lid of an extraction vessel. The solution to be extracted was poured into the vessel, which contained a metal stir bar. The lid was immediately screwed tightly to the glass, and the solution was stirred using a ceramic-topped magnetic stir plate. To ensure all the solutions were stirred at similar rates, the height of each vortex was measured. Stir rates were then adjusted until the heights were equal. All extraction volumes were 250 mL.

Following an extraction, the copolymer film/holder assembly was removed from the extraction vessel. Droplets of water adhering to the film surface were blotted with a Precision Wipe (Kimberly Clark, Roswell, GA). The film holder was then placed in the sample compartment of the spectrometer, and an IR spectrum of the film with the partitioned analytes was acquired. Fourier transformation of the sample spectrum ratioed to the background spectrum yielded an absorbance spectrum of the extracted analytes. The absorbance spectrum of a blank water extraction was then subtracted from each resultant standard/sample absorbance spectrum. This subtraction function is a programmed feature of WinFirst software. Quantitative data were determined by measuring the heights of the absorbance bands.

Extraction Procedures for Aqueous Samples. Standard solutions of 2,4,6-trinitrotoluene and 4-amino-2,6-dinitrotoluene were prepared in distilled water and extracted in the same manner as the spiked natural water solutions. A 250-mL volume of the standard or spike aqueous solution was extracted three times with dichloromethane in a 500-mL separatory funnel. Final extracted volumes were 100 mL. Concentrations of the spiked natural water samples were

determined from a calibration curve of GC peak area response versus extracted standard concentration.

Extraction Procedures for Soil Samples. The EPA-specified method for analysis of nitroaromatics by HPLC was used as a guideline with respect to the selected time frame of extraction (12). In all other aspects, however, the extraction conditions were not necessarily ideal for optimal recovery of analyte from the soil sample.

Two different solutions were used to extract 0.3-g portions of the TNT-contaminated soil sample. The first extraction was performed by stirring the soil in 1 L of distilled water containing 5% methanol for an 18-h time period. Three replicate 1-L dilutions in distilled water were prepared from 100 mL aliquots of this extract solution. A second soil portion was stirred for 18 h in 10 mL of 100% methanol. Three replicate 1-L dilutions in distilled water were prepared from 1 mL aliquots of the resultant extract. Each of these six extract dilutions was analyzed by SPME/IR and $\text{CH}_2\text{Cl}_2/\text{GC}$ as described for the spiked aqueous solutions.

A 2-g portion of the HMX/RDX-contaminated soil sample was stirred for 18 h in 10 mL of 100% methanol. Three replicate 1-L dilutions in distilled water were prepared from 1 mL aliquots of the resultant extract. Each of these dilutions was also analyzed by SPME/IR and $\text{CH}_2\text{Cl}_2/\text{GC}$ as described for the spiked aqueous solutions.

Results and Discussion

Silicone Polycarbonate Copolymer. MEM-213 is a semi-permeable membrane film that has several uses in medical and environmental instrumentation. As received from the manufacturer, it is a visually transparent film that is highly polished. Consequently, as discussed in previous work from our laboratory, its IR spectrum exhibits a sinusoidal modulation arising from the internal interference of the infrared radiation as it passes through the film (11). This "fringing" results in a serious degradation of the detection limit. It is, therefore, necessary to abrade the film prior to use by sanding both sides in order to eliminate the smooth, parallel surfaces. The membrane film is, however, quite flexible and will tolerate only light pressure while sanding. Excessive sanding also causes a decreased light throughput due to scattering and a resultant increase in the limit of detection (11). Thus, the films were abraded to yield a final baseline absorbance ranging from 0.1 to 0.15 AU in the region of 4000–3000 cm^{-1} .

It should be pointed out that, although abrasion of the film pieces eliminated "fringing" prior to extraction, these baseline modulations were again observed following extraction. By measuring the separation between successive "fringes", it was calculated that the film had become thicker during the extraction procedure, probably from water absorption. This new thickness thus created a new interference pattern. Infrared bands attributed to water absorbances were clearly visible in all the spectra after extraction. This phenomenon had other consequences that will be explained in the section on analytical band selection.

One possible solution for the problem of "fringing" after extraction was to use a thicker film. At the time this copolymer film was purchased, small sheets of the material were available in only one thickness. Membrane Products Co. did advertise this product in a 76.2- μm (0.003-in.) thickness, but it was only sold in very large quantities. We were unable to obtain even scraps of the 76.2- μm film. Because a solid phase of greater thickness was critical to the method development, we decided to create our own version of a thicker film. Product descriptions of MEM-213 published by the company indicated pieces of this polymer could be annealed together with heat, thus creating sheets of different sizes and shapes. We reasoned this process might also be used to form a thicker film piece. Positioning of the film squares between metal disks provided an even distribution of heat, and the c-clamp

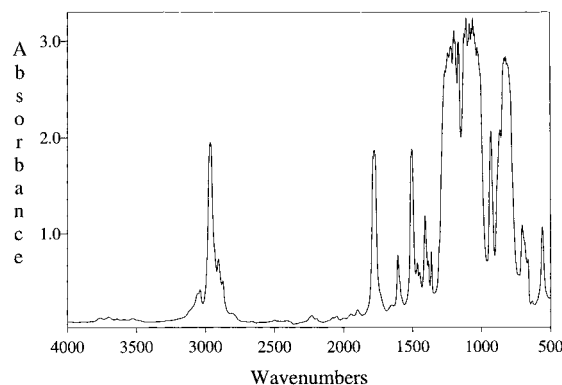


FIGURE 1. Infrared absorbance spectrum of 61.2 μm thickness MEM-213 following abrasion with sandpaper.

applied the necessary pressure. The two film squares were evenly fused following the heating procedure with no visible air space. Caliper measurements of film thickness indicated there was some compression due to pressure applied by the clamp. These thicker films averaged 61.2 μm or 0.0024 in. ($n = 25$).

Analytical Band Selection. Figure 1 is an absorbance spectrum of the 61.2 μm thickness MEM-213 copolymer film from 4000 to 500 cm^{-1} . Optically clear regions of the MEM-213 infrared spectrum include 4000–3000 cm^{-1} , 2860–1820 cm^{-1} , 1730–1620 cm^{-1} , 1585–1525 cm^{-1} , 1480–1420 cm^{-1} , 1360–1300 cm^{-1} , 750–715 cm^{-1} , 655–575 cm^{-1} , and 540–420 cm^{-1} . Small film absorptions occur in the regions of 714–656 cm^{-1} and 574–541 cm^{-1} . The remaining regions absorb infrared radiation strongly and are therefore opaque.

The spectral regions of 1585–1525 cm^{-1} and 1360–1300 cm^{-1} were used for determination of the nitroaromatic compounds. They encompass the aromatic- NO_2 symmetric (1360–1290 cm^{-1}) and asymmetric (1550–1500 cm^{-1}) stretching vibrations (13). Table 1 shows the IR absorbance bands for the various compounds tested in the study. Since the asymmetric vibration is the dominant absorbance for nearly all the compounds examined, it was most frequently selected as the major analytical band. The only exception was nitrobenzene, for which the asymmetric and symmetric vibrations were of approximately equal absorbance. There is an additional advantage of choosing the symmetric vibration as the analytical band for both nitrobenzene and 2-nitrotoluene. The asymmetric vibration of both compounds is in close proximity to a strong IR absorbance band of the copolymer film. Quantitative measurements of absorbance height are thus more difficult in this region at low analyte concentration levels.

As previously described, MEM-213 was found to absorb a small amount of water during the extraction procedure. A series of absorbance bands attributable to water was observed in the 1880 cm^{-1} –1390 cm^{-1} region of each IR spectrum. Because the NO_2 asymmetric vibration is located within this region, there was interference from water absorptions at low nitroaromatic concentration levels. It was therefore necessary to subtract an absorbance spectrum of a blank water extraction from each standard/sample absorbance spectrum. The symmetric vibration is not within the region of water absorptions and would be the preferred analytical band in cases where both vibrations are of equal intensity.

Each compound examined in this study exhibited a unique series of absorption bands in the out-of-plane region of the IR spectrum. Overlays of spectra for five nitroaromatic compounds in the range of 760–650 cm^{-1} are shown in Figure 2A,B. The bands in this region are due to interaction of NO_2 and C–H out-of-plane bending frequencies for aromatic hydrocarbons (13). Although these absorptions are not as

TABLE 1. Analytical Bands of Selected Nitroaromatic Compounds in Silicon Polycarbonate Copolymer (MEM-213)

compound	analytical band, ^a cm ⁻¹	alternate bands, cm ⁻¹ (intensity of analytical band, %)
nitrobenzene	1347	680 (11), 705 (45), 1527 (100), 2862 (2), 3076 (3), 3106 (1)
2-nitrotoluene	1525	666 (6), 729 (40), 1348 (60), 2860 (1), 3067 (2)
2,4-dinitrotoluene	1535	704 (5), 732 (17), 1346 (90), 3080–3111 (broad)
2,4,6-trinitrotoluene	1544	721 (12), 730 (7), 1346 (60), 1762 (7), 3100 (4)
4-amino-2,6-dinitrotoluene	1538	727 (12), 1311 (10), 1348 (16), 1355 (16), 1639 (20), 1758 (40), 3385 (15), 3485 (8)
2-amino-4,6-dinitrotoluene	1538	1347 (57), 3391 (13)

^a Strongest absorption band (except nitrobenzene – see text).

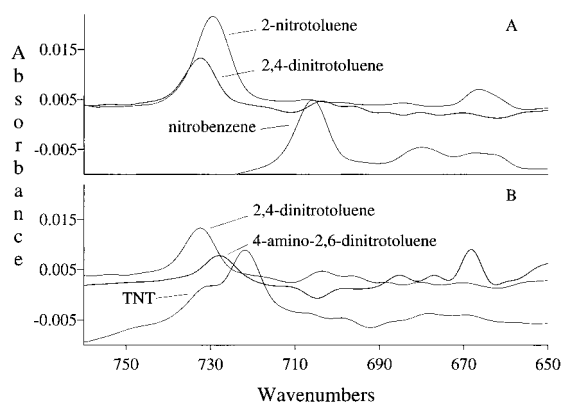


FIGURE 2. Comparative IR spectra of MEM-213 following extractions of water solutions containing 10 000 µg/L nitroaromatic compound. The absorbance bands are due to NO₂ and C–H out-of-plane bending for nitroaromatic components partitioned into the copolymer film. The spectrum of 2,4-dinitrotoluene was included in both 2A and 2B to serve as a reference.

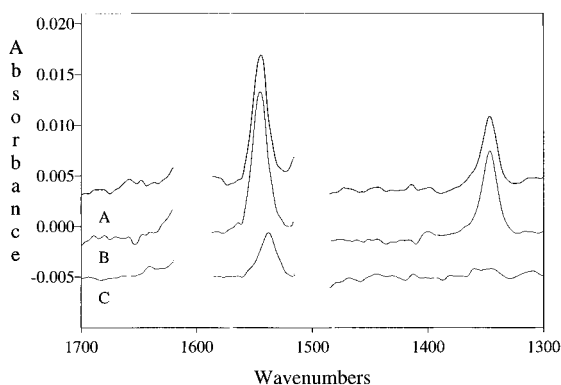


FIGURE 3. Infrared absorbance spectra of MEM-213 in the region of the NO₂ asymmetric and symmetric stretching vibrations. Spectra A and C were obtained from extraction of prepared aqueous solutions containing 1000 µg/L of TNT and 800 µg/L of 4-amino-2,6-dinitrotoluene, respectively. Spectrum B was obtained from extraction of a diluted soil sample extract containing TNT. Two sections of baseline have been removed from each spectrum due to the absorption of MEM-213 in those regions.

strong as the analytical bands, they could be an aid in identification of analytes that are present at higher concentration levels.

Analytical bands for all five nitroaromatic compounds occur in a fairly narrow range of frequencies. Since it is conceivable that more than one of these analytes may be present in an aqueous sample at any one time, there would probably be overlap of the absorptions used to determine the analytical concentrations. Figure 3 shows an overlay of three MEM-213 spectra in the region of the NO₂ asymmetric absorbance band following aqueous solution extractions. The 1544 cm⁻¹ band for TNT is evident in the spectrum from the

TABLE 2. Equilibration Times for Nitroaromatics in Silicone Polycarbonate Copolymer (MEM-213)

	time for 38.1 µm film, min.	time for 61.2 µm film, min.
nitrobenzene	30	45
2-nitrotoluene	30	45
2,4-dinitrotoluene	nd ^a	45
2,4,6-trinitrotoluene	30	50
4-amino-2,6-dinitrotoluene	nd ^a	45
2-amino-4,6-dinitrotoluene	nd ^a	45

^a Not determined, nd.

diluted soil sample extract (spectrum 3B). If an amine-dinitrotoluene product were also present, the band would appear larger and broadened. Spectra 3A and 3C are from prepared aqueous solutions of TNT and 4-amino-2,6-dinitrotoluene, respectively. These spectra demonstrate that analytical bands within six wavenumbers will thus overlap one another when both compounds are present. If the overlap prevented identification of individual bands, quantitative data could be based on total nitroaromatic species. Multivariate methods, such as partial least squares or principle component regression, may also be used to provide quantitative information of individual components in complex extraction mixtures.

The 4-amino-2,6-dinitrotoluene and 2-amino-4,6-dinitrotoluene compounds are, however, potentially distinguishable from the other nitroaromatic compounds due to the aromatic amine N–H stretching vibrations. The non-hydrogen bonded vibrations generally occur from 3400 to 3330 cm⁻¹ for the asymmetric band and from 3330 to 3250 cm⁻¹ for the symmetric band (14). The asymmetric band remained visible in MEM-213 spectra at aqueous solution concentrations of 800 µg/L.

Quantitative SPME/IR. Equilibration time studies indicated that partitioning of nitroaromatics from water into the MEM-213 solid phase required about 30 min for the 38.1 µm film. As shown in Table 2, equilibration times were not excessively lengthened for the 61.2 µm film. Quantitation limits, however, were improved by a factor of 2 with the thicker film. Thus, all of the quantitative data presented in this paper was obtained using a 61.2 µm film thickness.

Calibration information for six nitroaromatic compounds as obtained by SPME/IR is shown in Table 3. It should be noted that the upper linear ranges of calibration for 2,4,6-trinitrotoluene and 4-amino-2,6-dinitrotoluene were restricted by their water solubility. The ranges of the remaining three compounds, however, were restricted by the linearity of the infrared spectrometer. Limit of quantitation concentrations were determined from 2X the peak-to-peak baseline noise absorbance measured in the 1570–1524 cm⁻¹ and 1355–1320 cm⁻¹ spectral regions of blank water extractions ($n = 35$) (11). The quantitation limit of 2-amino-4,6-dinitrotoluene was estimated from the analytical data obtained for 4-amino-2,6-dinitrotoluene.

TABLE 3. SPME/IR Calibration Data for Nitroaromatic Compounds Following Extraction into Silicon Polycarbonate Copolymer (MEM-213)

	calibration data ^a			LDR, ^b $\mu\text{g/L}$	LOQ, ^c $\mu\text{g/L}$ (% RSD) ^d
	slope, (AU)/ ($\mu\text{g/L}$)	intercept, AU	r^2		
nitrobenzene	2.18×10^{-6}	$+4.07 \times 10^{-4}$	1.00	406–400000	400 (4)
2-nitrotoluene	5.15×10^{-6}	$+5.53 \times 10^{-4}$	1.00	200–151190	200 (4)
2,4-dinitrotoluene	5.29×10^{-6}	$+8.50 \times 10^{-4}$	0.999	80–100000	80 (3)
2,4,6-trinitrotoluene	1.09×10^{-5}	$+1.30 \times 10^{-3}$	1.00	50–24960	50 (5)
4-amino-2,6-dinitrotoluene	4.19×10^{-6}	$+1.26 \times 10^{-3}$	0.999	200–11945	200 (7)
2-amino-4,6-dinitrotoluene				nd ^e	$\sim 300^f$

^a Analytical absorbance band. ^b Tested linear dynamic range. ^c Limit of quantitation. ^d Percent relative standard deviation obtained from triplicate extractions. ^e Not determined, nd. ^f Value estimated from 4-amino-2,6-dinitrotoluene analytical data.

TABLE 4. Analytical Data for Spiked Natural Water Samples

	concentration, $\mu\text{g/L}$ (%RSD) ^a	
	SPME/IR ^b	CH ₂ Cl ₂ extraction/GC
2,4,6-trinitrotoluene		
0.25 mg/L	248 (1.9)	237 (3.3)
1 mg/L	940 (2.3)	969 (1.5)
4-amino-2,6-dinitrotoluene		
0.90 mg/L	910 (4.7)	887 (8.2)

^a Relative standard deviation obtained from triplicate extractions. ^b Data obtained from analytical absorbance band.

Application to Natural Water Samples. Liquid–liquid extraction with dichloromethane followed by gas chromatographic analysis was used to determine the definitive analyte concentrations in all the spiked water samples. This technique is considered to be a standard method for the analysis of nitroaromatic compounds in aqueous solutions and was, therefore, chosen to provide reference results (15). Both 2,4,6-trinitrotoluene and its transformation product 4-amino-2,6-dinitrotoluene were chosen since they are most relevant to explosives detection. A comparison of the analyzed concentrations obtained for the spiked solutions by CH₂Cl₂ extraction/GC and by SPME/IR is presented in Table 4. It is apparent that the two methods compare reasonably well. SPME/IR concentrations ranged from 97 to 105% of those obtained by GC analysis.

Natural water samples may contain other extractable compounds with IR spectra that could obscure the analyte bands of interest. Although it is not possible to investigate all potential interferences, a few examples are noted. It is known that the C=S stretching vibration occurs in the same spectral region as the NO₂ asymmetric absorbance band. An attempt was made to extract carbon disulfide from an aqueous solution, but this compound did not partition into MEM-213. Trifluralin, an herbicide that has two aromatic-NO₂ moieties, did partition into the copolymer film. Its symmetric and asymmetric absorbance bands occur at 1352 and 1540 cm⁻¹, respectively. The presence of this compound in a natural water sample would, however, be identifiable by the strong C–F stretching vibration at 1310 cm⁻¹.

Application to Soil Samples. Analyzed concentrations obtained for TNT from diluted soil extracts by SPME/IR and the reference CH₂Cl₂/GC method are shown in Table 5. SPME/IR concentrations ranged from 102 to 112% of those obtained by GC analysis. There is thus good agreement between results of the SPME/IR and CH₂Cl₂/GC analysis methods for both the aqueous/methanol and 100% methanol soil extractions. This demonstrates that SPME/IR is not affected by the choice of solution used in the extraction procedure. Although it is not the intent of this project to present a soil analysis method, it is clear that extraction with 100% methanol provided better recovery for TNT. Other research has confirmed that the choice of extractant and the method of extraction are

TABLE 5. Analytical Data for Soil Sample Extracts

	concentration, $\mu\text{g/L}$ (%RSD) ^a	
	SPME/IR ^b	CH ₂ Cl ₂ extraction/GC
2,4,6-trinitrotoluene		
water/5% methanol	1150 (2.4)	1130 (2.9)
100% methanol	2410 (2.9)	2150 (1.5)
RDX/HMX		
100% methanol	no IR absorbance bands	

^a Relative standard deviation obtained from triplicate extractions. ^b Data obtained from analytical absorbance band.

important when quantitative recovery of TNT from soil is the objective (16, 17). These experiments indicated, for instance, that use of an ultrasonic bath was a more effective technique for complete extraction than mechanical stirring. Analyte desorption rates were also affected by the type of soil and/or TNT concentration levels. Resultant recoveries were lower for soils with a high organic content that contained low concentrations of TNT.

It should be noted that our attempts to extract RDX with MEM-213 were unsuccessful. Although the compound has three NO₂ moieties, no absorbance bands were observed following extraction of aqueous solutions prepared at concentration levels of 1000 $\mu\text{g/L}$. There were also no absorbance bands in the IR spectrum of MEM-213 following a 60-min extraction of the diluted RDX/HMX methanol extract from soil. It is reasonable to assume that since RDX and HMX are only extractable by polar solvents, these compounds do not readily partition into the copolymer solid phase. Published octanol–water partition coefficients (log K_{ow}) for RDX and HMX are 0.87 and 0.061, respectively (18, 10), while the log K_{ow} for nitrobenzene, by contrast, is 1.83 (18). These constants tend to support the hypothesis. Although it might be desirable to determine both TNT and RDX simultaneously, it could also be considered an advantage that the MEM-213 solid phase is exclusive for nitroaromatic compounds. Perhaps a more polar solid phase would provide the opportunity to use SPME/IR for screening of nitramine compounds.

One final observation should be conveyed. The silicone polycarbonate copolymer membrane was found to be quite soluble in nearly every neat organic solvent except methanol. It therefore would not be suitable for aqueous samples that contain a high solvent concentration.

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